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CERAMIC PIGMENTS FOR PRODUCING BLACK GLAZES

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A new black-color ceramic pigment has been developed on the basis of the $CoO – Fe_2O_3$ system under a decreased temperature of synthesis (1000 – 1200°C). The optimum temperature range of the spinel-forming reaction in the specified oxide system is determined. When the obtained pigment is introduced into raw glaze for sanitary ceramics in milling, the resulting glaze coatings have intense and stable black color within a sufficiently wide interval of firing temperatures.

White glaze coatings are extensively used in the production of sanitary ceramics. By using tinted glazes, in particular, black glazes one can significantly expand available raw materials for ceramics and the product range.

Black-color glazes are mainly produced by introducing ceramic pigments synthesized at high temperatures (up to 1300°C) [1]. The color of glaze coating in this case substantially depends not only on the chemical-mineralogical composition of colorants and the temperature-time conditions of firing glazed products, but also on the acid-base properties of the silicate melt.

In the present study to produce black glaze coatings we used raw transparent glaze for sanitary porcelain ware [2] and initially tested well-known industrial ceramic pigments: Dulevskii (1063), Voronezhskii (VK-73), and Kievskii (220). The specified pigments were introduced in the amount of 6 weight parts (above 100 wt.%) of the mineral component of the glaze. Experimental suspensions were applied by casting on ceramic samples made of a porcelain mixture, which were dried and fired at a temperature of 1200°C with an isothermic exposure for 1 h.

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The analysis of results (Table 1) showed that none of the tested pigments introduced in the reference glaze ensures the formation of a black tint, which is corroborated by the brown color of coatings and a high diffuse reflection coefficient: 6.03 – 9.30% (this parameter characterizes the degree of blackness of a body). This circumstance corroborated a significant effect of the chemicomineralogical composition of the reference raw glaze mixture on the color of the fired pigment-bearing glaze layer and supports the opinion of the authors in [3] on the inevitable corrosion of a pigment in a glaze melt and subsequent formation of more stable compounds which in this particular case produce brown and not black color.

Consequently, it is necessary to develop a ceramic pigment that would ensure an intense black tint of a glaze coating based on the raw porcelain glaze for sanitary ceramic ware.

Black pigments are usually produced firing batches consisting of oxides of iron, cobalt, chromium, manganese, nickel and copper mixed in certain ratios. It is also known [2] that cobalt salt that is soluble in water can be used to effectively control the intensity and stability of black color in the pigment-bearing glaze layer.

TABLE 1

Coating parameters	Black pigment					
	57*	63*	90*	1063	VK-73	220
Coefficient of reflection:						
diffuse	7.10	6.03	8.66	6.57	9.30	7.00
mirror (luster)	82	80	86	91	90	87
Color (visually)	Brown with purple shade	Dark brown	Brown	Brownish-green	Brown	Brownish

* Based on data from [2].

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All this suggests that ceramic pigments should be introduced with an increased content of cobalt oxides, in order to produce an intense black color in feldspar glazes for sanitary ceramics. Considering this, as well as availability and a relatively low cost of iron oxides compared with other colorant oxides, it is interesting to study the possibilities of developing a black ceramic pigment in the binary system $CoO – Fe_2O_3$ (Fig. 1)

The conditions of the formation of ferrocobalt spinel were first investigated by Robin and Benar [4] who demonstrated that solid solutions of cobalt and iron oxalates in their thermal decomposition (300°C) produce a continuous series of metastable solid solutions γ-Fe_2O_3 and Co_3O_4 with the spinel structure. These solutions at a temperature above 500°C disintegrate depending on the system composition: mixed oxides with atomic content of cobalt ranging from 0 to 33% decompose into spinel $CoFe_2O_4$ and hematite α-Fe_2O_3. With increasing temperature, the specified binary range becomes narrower. The disintegration of solid solution γ-$Fe_2O_3 – Co_3O_4$ is related to the irreversible transformation of the cubic modification γ-Fe_2O_3 into the rhombohedral α-modification [4]. Mixed oxides with atomic content of Co ranging from 50 to 91% disintegrate into two spinel phases, which at a temperature of 800 – 860°C mutually dissolve and form a homogeneous spinel field.

A further increase in temperature is accompanied by the disintegration of cobalt-rich spinels into two phases: wustite and spinel phases (the latter has a higher concentration of iron than the initial spinel).

It also follows from the diagram (Fig. 1) that replacing part of cobalt in Co_3O_4 by iron increases the thermal stability of spinel at $P_{O_2} = 0.21$ atm and $P_{tot} = 1.01$ atm [4].

According to published data, the main chromophore in this system to produce a required tint in the glaze layer has to be cobalt ferrite $CoFe_2O_4$ that has a black-gray color. This compound crystallizes in the cubic system [5] and can be categorized as spinel of type 1 according to Tumanov's classification [6]. The authors in [7] also note the possibility of producing cobalt ferrite from a mixture of crystalline reactants and or boiling precipitated hydroxides.

The synthesis of the considered spinel from crystalline reactants is simpler, therefore, was used by us in developing a black ceramic pigment.

The possibility of reaction between the components of the experimental ceramic pigment can be inferred by the thermodynamic probability of the chemical reaction of the formation of cobalt ferrite from iron and cobalt oxides:

$$CoO + Fe_2O_3 = CoFe_2O_4.$$

Based on estimated data, the temperature dependence of the isobaric-isothermal potential ΔG of the spinel-formation process has been constructed (Fig. 2).

The analysis of this dependence shows that as the firing temperature of the experimental pigment grows, the probability of cobalt ferrite formation increases, however, the values ΔG in a rather wide temperature interval vary insignificantly. Thus, ΔG of the reaction at 1073 K is equal to – 7.41 kcal/mole and at 1573 K it is – 9.09 kcal/mole, which suggests the possibility of cobalt ferrite formation at relatively low temperatures as well. The results of our calculations agree with data in [4, 8].

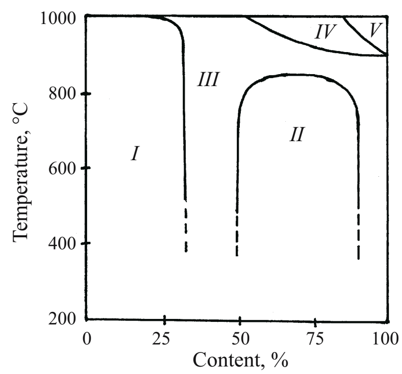

Fig. 1. Phase diagram of system $CoO – Fe_2O_3$ [4]: *I*) α-Fe_2O_3 + spinel enriched with iron, *II*) spinel enriched with iron + spinel enriched with cobalt; *III*) spinel; *IV*) spinel enriched with cobalt + solid solution (Co, Fe)O; *V*) solid solution based on cobalt (II) oxide.

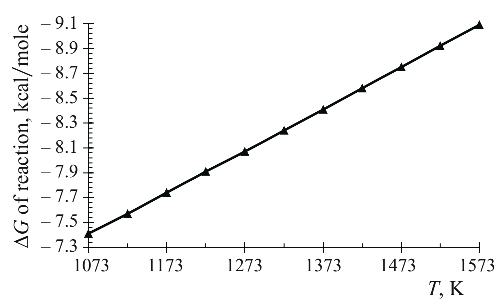

Fig. 2. Dependence of isobaric-isothermal potential ΔG of the reaction $CoO + Fe_2O_3 = CoFe_2O_4$ on temperature *T*.

Thus, thermodynamic calculations corroborate the possibility of producing spinel $CoFe_2O_4$ in the system $CoO – Fe_2O_3$ under normal atmospheric pressure.

The batch materials for the experimental ceramic pigment are cobalt oxide and iron scale taken in the ratio of 1 : 1. The synthesis of the pigment was carried out within the temperature interval of 800 – 1300°C with 1-h exposure at the maximum temperature.

The differential thermal analysis of the experimental pigment mixture exhibits the presence of two exothermic and one endothermic effect. The exothermic effect at the temperature of 310°C is related to the oxidation of magnetite Fe_3O_4 and wustite FeO, which prevail in the composition of rolled steel scale, to magnetite γ-Fe_2O_3 and hematite α-Fe_2O_3, respectively. The exothermic effect with the maximum at 530°C is presumably determined by the reaction between iron and cobalt oxides with the formation of cobalt ferrite

TABLE 2

Crystalline phase	Phase composition of black pigment, wt.%, at temperature of synthesis, °C			
	800	1000	1200	1300
$CoFe_2O_4$	31.0	75.0	87.5	82.0
α-Fe_2O_3	23.5	5.0	–	–
Co_3O_4	45.5	20.0	12.5	18.0

crystals, whose presence in the synthesized pigment is corroborated by x-ray phase analysis. The endothermic effect at 970°C is presumably due to the dissociation of Co_3O_4, which is also present in the composition of cobalt (II) oxide selected for the experiment, and its transformation into CoO.

The phase composition of the black ceramic pigment powder obtained at 800 – 1300°C (Table 2) is mainly represented by cobalt ferrite $CoFe_2O_4$ and also by hematite α-Fe_2O_3 and cobalt oxide Co_3O_4.

The x-ray phase analysis of the experimental pigment helped to determine the optimum firing temperatures, namely 1200°C, at which the maximum quantity of the main chromophore (cobalt ferrite) is formed (about 87.5 wt.%).

The phase composition of the pigment synthesized at 800°C, namely the high content of α-Fe_2O_3 and Co_3O_4 (around 23.5 and 45.5 wt.%, respectively) indicates that the process of spinel formation is not completed. Firing at 1000°C with 60 min exposure does fully complete the binding of iron oxide into a spinel either (the weight content of residual α-Fe_2O_3 is about 5%). Apparently, at the firing temperature of 1300°C the dissociation of $CoFe_2O_4$ takes place, which is observed in [4] and also corroborated by the decreased intensity of the main peaks on the diffraction patterns corresponding to cobalt ferrite and the intensification of Co_3O_4 peaks. Magnetite was not identified in the course of dissociation, since its crystalline lattice has the same type as cobalt ferrite lattice [8]. The decomposition of $CoFe_2O_4$, in the opinion of Tret'yakov [4], can be significantly decelerated by two ways: by abruptly increasing oxygen pressure in the gaseous phase or by lowering the temperature of synthesis. The latter is confirmed by the results of our experiments: decreasing the firing temperature for the experimental pigment to 1200°C has a favorable effect on the stability of emerging spinel $CoFe_2O_4$.

The firing of glaze coating containing 6 weight parts of black pigment was carried out at 1150 – 1250°C. The optimum results were achieved using the experimental pigment synthesized in the temperature interval of 1000 – 1200°C. The glazes containing this pigment have good spreading over a ceramic base and a steady saturated black color (diffuse reflection coefficient 2.63 – 2.85%) [9]. The color tone of developed glaze coating is within the range of 565 – 577 nm and corresponds to the purple spectrum range, the color purity is 1 – 3%, and the luster is 90 – 93%.

Thus, the possibility of synthesizing black ceramic pigments based on $CoO – Fe_2O_3$ system at decreased temperatures (below 1200°C) has been demonstrated.

It is advisable to use the developed pigment to produce high-quality black glaze coating for sanitary porcelain ware within a sufficiently wide firing interval: 1150 – 1250°C.

REFERENCES

1. I. V. Pishch and G. N. Maslennikova, *Ceramic Pigments* [in Russian], Vysshaya Shkola, Minsk (1987).
2. Ya. I. Belyi, A. V. Zaichuk, N. F. Smakota, and É. V. Gololobov, "Glaze coatings of dark colors for sanitary ceramic ware," *Vopr. Khim. Khimich. Tekhnol.*, No. 6, 47 – 49 (2002).
3. H. Murdock Stephen and A. Eppler Richard, "The interaction of ceramic pigments with glazes," *Ceram. Engl.*, **10**(1 – 2), 81 – 86 (1989).
4. Yu. D. Tret'yakov, *Thermodynamics of Ferrites* [in Russian], Khimiya, Leningrad (1967).
5. A. A. Shchepetkin, *Physicochemical Analysis of Oxides of Variable-Valence Metals* [in Russian], Nauka, Moscow (1987).
6. S. G. Tumanov, "New ways for synthesis and classification of ceramic pigments," *Steklo Keram.*, No. 6, 36 – 38 (1967).
7. P. P. Budnikov and A. M. Ginstling, *Reactions in Mixtures of Solid Materials* [in Russian], Stroiizdat. Moscow (1971).
8. Yu. D. Tret'yakov and K. G. Khomyakov, "Oxygen activity above solid solutions of cobalt ferrite with magnetite," *Zh. Neorg. Khim.*, **VIII**(11), 2569 – 2572 (1963).
9. Ya. I. Belyi and A. V. Zaichuk, "The problem of producing black glaze coating for fine ceramic products," in: *Proc. Inter. Conf. "Latest Achievements in Replacing Imported Products for Chemical Industry and Construction Materials"* [in Russian], Minsk (2003), pp. 93 – 95.